

Molecular Factors Governing the Miscibility of Polymer Blends (Invited)

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Despite the important contributions to our understanding of the thermodynamics of polymer blends by Flory-Huggins and various equation of state models, all these venerable approaches ignore the fact that much of the gross and subtle thermodynamic behaviors of polymer systems are governed by the synergistic variations of the effective interaction parameters χ_{ij} with temperature, blend and copolymer composition, chain architecture, pressure, etc., variations whose molecular underpinnings are completely absent in these theories. The lattice cluster theory (LCT) alleviates many of these severe deficiencies through two significant theoretical advances. Firstly, the standard lattice model of polymer systems is extended to permit monomers (and solvent molecules if solvent is present) to have specific structures, dictated by united atom group models, and therefore to occupy several lattice sites. This extension is combined with a vastly superior systematic solution of the structured monomer lattice model, thereby providing a molecular theory for the miscibility of polymer blends. Illustrative applications of the theory are described, including an explicit method for computing the previously enigmatic “entropic” contribution χ_s to the effective interaction parameter, a quantitative realization of the previously vague notion of “surface” fractions, the prediction (prior to observations) of the pressure dependence of the χ parameter and hence of blend phase diagrams, the importance of monomer molecular structures in controlling phase diagrams, and more. While the full (compressible system) theory is required to such as the pressure dependence, a simplified high molecular weight, incompressible limit is derived study phenomena as useful for establishing general trends. Both versions of the LCT are illustrated by analyzing the observed pressure dependence of blend properties, the strong influence of monomer molecular structure on the miscibility of polyolefin blends, a new mechanism for the occurrence of lower critical solution temperature phase diagrams in polymer blends, the unusual trends observed for the miscibility of norbornene-co-ethylene binary mixtures, and the remarkable oscillation of polystyrene-b-poly(n-alkyl methacralate) block copolymers between systems ordering on cooling and on heating as n is varied.